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10/540866
JC17 Rec'd PCT/PTO 27 JUN 2005

DESCRIPTION

5 EXPANDABLE BEADS OF STYRENE-MODIFIED LINEAR
LOW-DENSITY POLYETHYLENE-BASED RESIN, PRODUCTION
METHOD THEREFOR, PRE-EXPANDED BEADS AND
EXPANDED MOLDED ARTICLE

Technical Field

10 The present invention relates to expandable beads of a styrene-modified linear low-density polyethylene-based resin, production method therefore, pre-expanded beads and expanded molded article.

Background Art

15 A polyethylene-based resin foam is generally used as a packing material owing to its high resilience and excellent oil and impact resistance. The polyethylene-based resin foam, however, has drawbacks that its stiffness and compressive strength are low. On the other hand, a polystyrene-based
20 resin foam is excellent in stiffness, but has a drawback that it is brittle.

To overcome such drawbacks, Japanese Examined Patent Publication No. SHO 51(1976)-46138, Japanese Examined Patent Publication No. SHO 52(1977)-10150,
25 Japanese Examined Patent Publication No. SHO

58(1983)-53003, and Japanese Unexamined Patent Publication No. SHO 62(1987)-59642 disclose methods for obtaining expandable beads of a styrene-modified polyethylene-based resin by impregnating a styrene monomer into a
5 polyethylene-based resin for polymerization.

Examples of the polyethylene-based resin used in the method substantially include low-density polyethylene, high-density polyethylene, and an ethylene-vinyl acetate copolymer. However, where these resins are used, styrene is
10 not sufficiently dispersed into polyethylene, and thus polyethylene needs to be cross-linked to provide sufficient stiffness and impact resistance. The cross-linking of polyethylene, however, causes a gel component comprising a cross-linked polymer to be generated.

15 To solve the above-mentioned problem, Japanese Patent No. 2668384 discloses a method for obtaining an expanded molded article of a modified polyethylene-based resin excellent in stiffness and impact resistance. In this method, 100 parts by weight of non-crosslinked linear low-density
20 polyethylene-based resin beads, 5 to 300 parts by weight of a vinyl aromatic monomer, and 1 to 3 parts by weight of a polymerization initiator relative to 100 parts by weight of the vinyl aromatic monomer are dispersed in an aqueous medium. Then, a suspension thus obtained is heated at such a
25 temperature that polymerization of the monomer does not

substantially take place for impregnation of the monomer into an inside and a surface of the polyethylene-based resin beads. Subsequently, the temperature of the suspension is raised to polymerize the monomer, as a result the expanded molded
5 article of the modified polyethylene-based resin is obtained by micro-dispersed of a vinyl aromatic polymer in polyethylene.

In this method, however, the polymerization is carried out after the monomer is fully impregnated into polyethylene. Accordingly, a monomer content in polyethylene is limited.
10 When a large amount of the monomer needs to be impregnated into polyethylene, there is a problem that the remaining monomer which is unimpregnated into polyethylene is polymerized and that a large amount of polymer powder is generated. Also, where a ratio of polyethylene to the vinyl
15 aromatic polymer is high, a retention of a blowing agent is poor and thus a reduction in density of the expanded molded article is difficult. Furthermore, since an amount of the polymerization initiator used in the method is as high as 1 to 3 parts by weight, a molecular weight of the vinyl aromatic
20 polymer is small, making it difficult to provide a molded article having a sufficient strength.

In Examples of the above-mentioned patent, a styrene monomer is added to linear low-density polyethylene-based resin beads having a melting point of 122 °C for
25 polymerization at 115 °C (the melting point of the resin beads

is not specified in Examples, but the present inventors confirmed from the product name of the resin beads described in Examples that the beads have the above-mentioned melting point). The polymerization at this temperature often results
5 in graft polymerization of styrene monomer on a polyethylene chain. Consequently, in a resin obtained, a gel component derived from cross-linking is not generated, but instead, a gel component derived from the graft polymerization is generated. Hereinafter, the term "graft polymer" means a gel component
10 containing polystyrene, and the term "crosslinked polymer" means a gel component substantially not containing polystyrene.

Where styrene monomer is impregnated into a polyethylene-based resin for polymerization to obtain a resin
15 which is subsequently impregnated with a blowing agent and molded by heating to obtain an expanded molded article, polyethylene needs to be cross-linked as mentioned above for providing sufficient stiffness and impact resistance. However, when the expanded molded product thus obtained is collected
20 for recycled use thereof, a gel component generated by the cross-linking is contained in a molten resin of the expanded molded article, thereby causing the recycling of the expanded molded article to be difficult.

Accordingly, there has been desired development of
25 expandable beads of a styrene-modified linear low-density

polyethylene-based resin which are capable of widely changing a ratio of styrene monomer to polyethylene and suppressing generation of a gel component derived from cross-linking or graft polymerization, and which provide an expanded molded
5 article having sufficient strength.

Disclosure of Invention

The object of the present invention is to provide expandable beads of a styrene-modified linear low-density
10 polyethylene-based resin for production of an expanded molded article which has excellent impact resistance and physical properties and which can be readily recycled by minimizing generation of a gel component derived from graft polymerization etc. of styrene on a polyethylene chain.

15 The present inventors made an extensive study to achieve the above-mentioned object. Consequently, the present inventors found that by adopting linear low-density polyethylene and by adding a styrene monomer to polyethylene for polymerization at a specific range of temperatures under
20 the presence of a specific amount of an initiator, there are provided the expandable beads of a styrene-modified linear low-density polyethylene-based resin. The expandable beads thus obtained are not cross-linked, and provide an expanded molded article which sufficiently exerts toughness of
25 polyethylene and stiffness of polystyrene. Also, the

expandable beads do not generate the gel component that impairs recyclability of the expanded molded article. Thus, the present invention is completed.

According to the present invention, there is provided a
5 method for producing expandable beads of a styrene-modified linear low-density polyethylene-based resin comprising, in the order recited, the steps of:

dispersing 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin beads, 50 to 1000
10 parts by weight of a styrene-based monomer, and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer into a suspension containing a dispersant;

impregnating the styrene-based monomer into the
15 low-density polyethylene-based resin beads by heating a resultant dispersion at such a temperature that polymerization of the styrene-based monomer does not substantially take place;

performing polymerization of the styrene-based
20 monomer at a temperature of $(T-15)$ to $(T-8)$ °C or $(T+1)$ to $(T+5)$ °C (where T °C is a melting point of the low-density polyethylene-based resin beads); and

impregnating a volatile blowing agent into the resin beads during or after the polymerization,

25 whereby resin components of the expandable beads

contain a gel component comprising less than 2 wt% of a graft polymer.

According to another aspect of the present invention, there is also provided a method for producing expandable
5 beads of a styrene-modified linear low-density polyethylene-based resin comprising, in the order recited, the steps of:

dispersing 100 parts by weight of non-crosslinked linear low-density polyethylene-based resin beads, 30 to 300
10 parts by weight of a styrene-based monomer, and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer into a suspension containing a dispersant;

impregnating the styrene-based monomer into the
15 low-density polyethylene-based resin beads by heating a resultant dispersion at such a temperature that polymerization of the styrene-based monomer does not substantially take place;

performing a first polymerization of the styrene-based
20 monomer at a temperature of $(T-15)$ to $(T-8)$ °C or $(T+1)$ to $(T+5)$ °C (where T °C is a melting point of the low-density polyethylene-based resin beads);

adding a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by
25 weight of the styrene-based monomer when a conversion ratio

of polymerization reaches to 80 to 99.9%, and performing
impregnation of the styrene-based monomer into the
polyethylene-based resin beads and a second polymerization of
the styrene-based monomer at a temperature of (T-15) to
5 (T-8) °C or (T+1) to (T+5) °C (where T °C is a melting point of
the polyethylene-based resin beads) (wherein a total amount of
the styrene monomers used in the first and second
polymerizations is more than 50 parts by weight and not more
than 1000 parts by weight relative to 100 parts by weight of
10 the low-density polyethylene-based resin beads); and

impregnating a volatile blowing agent into the resin
beads during or after the polymerization,

whereby resin components of the expandable beads
contain a gel component comprising less than 2 wt% of a graft
15 polymer.

According to still another aspect of the present
invention, there is provided expandable beads of a
styrene-modified linear low-density polyethylene-based resin
comprising a volatile blowing agent and a base resin, the base
20 resin containing more than 50 to 1000 parts by weight of a
polystyrene-based resin component relative to 100 parts by
weight of a non-crosslinked linear low-density
polyethylene-based resin component, wherein the base resin
contains less than 2 wt% of a gel component comprising a graft
25 polymer of the polystyrene-based resin component and the

low-density polyethylene-based resin component.

According to further aspect of the present invention,
there is provided pre-expanded beads having a bulk density of
20 to 200 kg/m³, obtained by pre-expanding the
5 above-mentioned expandable beads of the styrene-modified
linear low-density polyethylene-based resin.

According to still further aspect of the present
invention, there is provided an expanded molded article having
a density of 20 to 200 kg/m³, obtained by expansion molding
10 of the above-mentioned pre-expanded beads.

Brief Description of Drawings

Fig. 1 is a graph showing a relationship between a
polymerization temperature and a gel fraction.

15

Best Mode for Carrying Out the Invention

An expandable beads of a styrene-modified linear
low-density polyethylene-based resin (hereinafter referred to as
expandable resin beads) obtained by the production method of
the present invention comprise a volatile blowing agent and a
20 base resin containing a non-crosslinked linear low-density
polyethylene-based resin component and a polystyrene-based
resin component.

As the non-crosslinked linear low-density
25 polyethylene-based resin component (hereinafter referred

simply to as a polyethylene-based resin component) used in the present invention, a copolymer of ethylene and an α -olefin can be mentioned.

Examples of the α -olefin include 1-butene, 1-pentene,
5 1-hexene, 3,3-dimethyl-1-butene, 4-methyl-1-pentene,
4,4-dimethyl-1-pentene, and 1-octene. Among those,
1-butene and 1-hexene are preferable.

A ratio of ethylene to the α -olefin may vary depending upon physical properties desired and preferably in a range of
10 1:0.01 to 1:0.1 (weight ratio). The term "low-density" means a density in a range of 0.910 to 0.925 g/ml.

Low-density polyethylene, high-density polyethylene, an ethylene-propylene copolymer, an ethylene-vinyl acetate copolymer and an ethylene-acrylic acid copolymer which have
15 a cross-link and/or a branched chain, and two or more types of these polymers may be used to such an extent that a desirable effect of the invention is not suppressed.

Examples of the polystyrene-based resin component include resin components derived from monomers such as
20 styrene, α -methylstyrene, vinyltoluene, and chlorostyrene.

An amount of the polystyrene-based resin component is 50 to 1000 parts by weight, and preferably 100 to 900 parts by weight relative to 100 parts by weight of the polyethylene-based resin component. Where the amount of
25 the polystyrene-based resin component is less than 50 parts by

weight, a characteristic of the polyethylene-based resin component, i.e., fine stiffness is hardly displayed. Furthermore, due to its poor retention of the volatile blowing agent, a reduction in density of an expanded molded product is difficult and expansion-moldability is reduced. Where the amount of the polystyrene-based resin component exceeds 1000 parts by weight, characteristics of the polyethylene-based resin component, i.e., high resilience and excellent oil and impact resistance are hardly displayed. Furthermore, since styrene is not sufficiently absorbed into an inside of the polyethylene-based resin component and is polymerized alone, a large amount of polymer powder is generated.

Especially, conventional methods have difficulty in producing the expandable resin beads uniformly containing not less than 300 parts by weight of the polystyrene-based resin component, whereas the present invention can easily produce them.

As the volatile blowing agent, for example, a hydrocarbon such as propane, butane, isobutene, pentane, isopentane, cyclopentane, and hexane may be used alone, or two or more types of these hydrocarbons may be used in combination.

A content of the blowing agent is preferably 5 to 10 parts by weight relative to 100 parts by weight of the resin component (an amount of the polyethylene-based resin

component and the polystyrene-based resin component in total) which constitute the expandable resin beads.

In the present invention, less than 2 wt% of the gel component (a gel fraction) comprising the graft polymer of the polyethylene-based resin component and the polystyrene-based resin component is contained in the base resin of the expandable resin beads. A criterion for judging whether or not the gel component is a graft polymer is the presence or absence of polystyrene in the gel component. In the present invention, the gel component containing 10 wt% or more of polystyrene is defined as the graft polymer. A method for determining a polystyrene content in the gel component is described in Examples.

The gel fraction within the above-mentioned range facilitates recycled use of the expanded molded product and allows for production of the expandable resin beads which provide the expanded molded product excellent in physical properties including impact resistance.

A gel fraction of 2 wt% or more is not preferable because where a resin is subjected to melt-kneading by an extruder for recycled use of the expanded molded article, the unmelted gel component forms a granular structure and thus a strand of resin extruded from the extruder is improperly cut immediately after it is extruded, rendering difficult the recycled use of the foamed molded article. The gel fraction

more preferably is 1.8 wt% or less. The strand of resin extruded from the extruder is normally cut into particles to be recycled.

5 Preferably, the expandable resin beads each have a substantially spherical shape or a cylindrical shape having an L/D (where L is a length of each bead and D is a diameter of each bead) of 0.6 to 1.6, and an average bead size of 0.3 to 2.0 mm.

10 The beads having a high ovality such that the L/D is not more than 0.6 and not less than 1.6 are not preferable since the expandable resin beads have poor mold fillability when they are pre-expanded as expandable styrene-modified resin beads and filled into a mold to obtain the expanded molded article. The shape of the expandable resin beads
15 preferably is substantially spherical to improve the mold fillability.

The average bead size of less than 0.3 mm is not preferable because a retention of the blowing agent decreases and a reduction of density of the formed molded article is
20 difficult. The average bead size of more than 2.0 mm is also not preferable since not only the beads have poor mold fillability, but also thinning of the formed molded article is difficult.

A production method for the expandable resin beads of
25 the invention will hereinafter be described.

Firstly, 100 parts by weight of the polyethylene-based resin beads, 50 to 1000 parts by weight of the styrene-based monomer, 0.1 to 0.9 parts by weight of the polymerization initiator relative to 100 parts by weight of the styrene-based monomer are dispersed in the suspension containing the dispersant.

Preferably, the polyethylene-based resin beads used in the method each have the substantially spherical shape or the cylindrical shape having an L/D (where L is a length of each bead and D is a diameter of each bead) of 0.6 to 1.6, and preferably have an average bead size of 0.2 to 1.5 mm. The polyethylene-based resin beads having a high ovality such that the L/D is not more than 0.6 and not less than 1.6 are not preferable since the polyethylene-based resin beads have poor mold fillability when they are pre-expanded as the expandable styrene-modified resin beads and filled into a mold to obtain the expanded molded article. The shape of the polyethylene-based resin beads preferably is substantially spherical to improve mold fillability. The average bead size of less than 0.2 mm is not preferable since a retention of the blowing agent decreases and a reduction of the density of the expanded molded article is difficult. The average bead size of more than 1.5 mm is also not preferable because not only the beads have poor mold fillability, but also thinning of the expanded molded article is difficult.

Examples of an aqueous medium which is a component of the suspension include water and a mixed medium of water and an aqueous solvent (e.g., a lower alcohol).

5 A dispersant is not particularly limited and any conventional dispersant may be used. Specifically, the dispersant may be practically insoluble inorganic substances such as calcium phosphate, magnesium pyrophosphate, sodium pyrophosphate, and magnesium oxide.

10 A polymerization initiator may be one that is generally used as a suspension polymerization initiator of the styrene-based monomer. Examples thereof include organic peroxides such as benzoyl peroxide, t-butyl peroxide, t-butyl peroxybenzoate, dicumyl peroxide, 2, 5-dimethyl-2, 5-di-t-butyl
15 peroxyhexane, t-butylperoxy-3, 5, 5-trimethylhexanoate, and t-butyl-peroxy-2-ethylhexyl carbonate. These polymerization initiators may be used alone, or two or more types of these polymerization initiators may be used in combination.

 An amount of the polymerization initiator is preferably
20 0.1 to 0.9 parts by weight, and more preferably 0.2 to 0.5 parts by weight relative to 100 parts by weight of the styrene-based monomer. The polymerization initiator in an amount of less than 0.1 parts by weight is not preferable since styrene is not smoothly polymerized, and thereby polystyrene and
25 polyethylene are not homogeneously mixed in the resin beads

and a larger amount of polymer powder is generated. Use of the polymerization initiator in an amount of more than 0.9 parts by weight decreases a molecular weight of the polystyrene-based resin.

5 A molecular weight of polystyrene-based resin component is preferably about 200,000 to 400,000 to achieve fine physical properties. The polymerization initiator in an amount of more than 0.9 parts by weight can only achieve a styrene molecular weight less than the above range.

10 The amount of the styrene-based monomer added in the suspension is 50 to 1000 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads.

Next, the resultant dispersion is heated to such a temperature that polymerization of the styrene-based monomer
15 does not substantially take place to impregnate the styrene-based monomer into the polyethylene-based resin beads.

An appropriate time required for impregnating the styrene-based monomer into the inside of the
20 polyethylene-based resin beads is 30 minutes to 2 hours, since when the polymerization proceeds before the styrene-based monomer is sufficiently impregnated into the resin beads, the polymer powder of polystyrene is generated. The temperature at which the styrene-based monomer is substantially not
25 polymerized should be higher to accelerate an impregnation

rate, but the temperature needs to be determined in due consideration of a decomposition temperature of the polymerization initiator.

Subsequently, the polymerization of the styrene-based monomer is carried out at a temperature of (T-15) to (T-8) °C or (T+1) to (T+5) °C (where T °C is the melting point of the above-mentioned polyethylene-based resin beads).

The polymerization temperature of lower than (T-15)°C is not preferable because a crystallized moiety of polyethylene is not sufficiently melted and the styrene-based monomer is not uniformly polymerized in the inside of the polyethylene-based resin beads. The polymerization at a temperature in a range of higher than (T-8)°C and lower than (T+1)°C is not preferable since a gel fraction of resultant expandable resin beads exceeds 2 wt%.

Furthermore, there may be a case where the gel fraction exceeds 40 wt% depending on the type and amount of the polymerization initiator and the polymerization temperature. The above-mentioned temperature range is a little lower than the melting point of the polyethylene-based resin beads, and crystals hardly exist at this temperature. However, since a polymer chain is not in free state, it is presumed that the styrene-based monomer is more likely to be graft-polymerized on the polyethylene chain.

In addition to the above, at a temperature of more

than (T+5) °C, an internal pressure of a polymerization reactor is increased, causing not only the addition of the styrene-based monomer to be difficult but also the gel component to be generated. It is presumed that, at such a high temperature, abstraction of a hydrogen atom from the polyethylene chain is more likely to occur and thus graft polymerization readily proceeds.

Lastly, the volatile blowing agent is impregnated into the resin beads during or after the polymerization so that the expandable resin beads are obtained. This impregnation of the blowing agent can be performed by a per se known method. For example, the impregnation during polymerization can be carried out by conducting the polymerization in a closed vessel, and by injecting the volatile blowing agent into the vessel.

The impregnation after the polymerization is carried out by injecting the volatile blowing agent into a closed vessel. In the impregnation after the polymerization, a vessel for the polymerization may not be a closed vessel as long as the impregnation is carried out in the closed vessel.

The above-mentioned method provides the expandable resin beads having excellent characteristics. However, where the amount of the styrene-based monomer to be added exceeds 300 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads, the amount of the polymer powder of polystyrene tends to increase.

More specifically, in the above-mentioned method,
where the amount of the styrene-based monomer is 50 to 300
parts by weight relative to 100 parts by weight of the
polyethylene-based resin beads, only a small amount of
5 polymer powder of polystyrene is generated and the expandable
resin beads having the most stable and excellent
characteristics are readily obtained.

Where the amount of the styrene-based monomer
exceeds 300 parts by weight, it is preferable that the
10 styrene-based monomer is impregnated into the
polyethylene-based resin beads in two separate steps as
described below to minimize the generation of the polymer
powder.

Firstly, 100 parts by weight of polyethylene-based
15 resin beads, 30 to 300 parts by weight of a styrene-based
monomer, and 0.1 to 0.9 parts by weight of a polymerization
initiator relative to 100 parts by weight of the styrene-based
monomer are dispersed in a suspension containing a
dispersant.

20 Then, a dispersion thus obtained is heated at such a
temperature that polymerization of the styrene-based monomer
does not substantially take place to impregnate the
styrene-based monomer into the polyethylene-based resin
beads.

25 Subsequently, a first polymerization of the

styrene-based monomer is performed at a temperature of (T-15) to (T-8) °C or (T+1) to (T+5) °C (where T °C is a melting point of the polyethylene-based resin beads).

In turn, when a conversion ratio of polymerization reaches to 80 to 99.9%, a styrene-based monomer and 0.1 to 0.9 parts by weight of a polymerization initiator relative to 100 parts by weight of the styrene-based monomer are added, and impregnation of the styrene-based monomer into the low-density polyethylene-based resin beads and a second polymerization of the styrene-based monomer are performed at a temperature of (T-15) to (T-8) °C or (T+1) to (T+5) °C (where T °C is the melting point of the polyethylene-based resin beads). The amount of the styrene-based monomer used in the first and second polymerization in total is 50 to 1000 parts by weight relative to 100 parts by weight of the polyethylene-based resin beads.

Where more than 300 parts by weight of the styrene-based monomer is added when the conversion ratio of polymerization reaches to 80%, the styrene-based monomer is quickly impregnated into the polyethylene-based resin beads for quick polymerization of the styrene-based monomer, whereby the generation of the polymer powder of polystyrene can be suppressed. When the conversion ratio of polymerization exceeds 99.9%, the impregnation of the styrene-based monomer added is difficult and a conversion

ratio decreases, causing the generation of the powdered beads difficult to be suppressed.

A mixed solution containing the styrene-based monomer and the polymerization initiator may be added continuously or intermittently for the second polymerization. To prevent the generation of the polymer powder, the impregnation into the inside of the polyethylene-based resin beads and the polymerization are preferably performed at almost the same time. A fast addition rate is not preferable because the fast addition rate in combination with a relatively high polymerization temperature causes the polymerization to occur before the resin beads are impregnated. An extremely slow addition rate is not preferable since it may hinder the polymerization. For example, the addition rate for 300 to 1000 parts by weight of the styrene-based monomer is 3 to 5 hours.

Lastly, a volatile blowing agent is impregnated into the resin beads during or after the polymerization in the same manner as in the above-mentioned production method, so that expandable resin beads are obtained.

The expandable resin beads of the present invention thus obtained may serve as pre-expanded beads by pre-expanding the expandable resin beads to a predetermined bulk density (e.g., 20 to 200 kg/m³) by a conventional method. A method for determining the bulk density will be described in

Examples.

Furthermore, an expanded molded article is provided by filling the pre-expanded beads into a mold and heating the pre-expanded beads again to allow them to fuse together by
5 heat while expansion.

As a medium for heating the pre-expanded beads, steams are suitably used. A density of the expanded molded article is preferably 20 to 200 kg/m³. The expanded molded article having a density of less than 20 kg/m³ is not preferable
10 since sufficient strength is not achieved. The expanded molded article having a density of more than 200 kg/m³ is also not preferable since reduction in weight can not be achieved and the expanded molded article may not be able to sufficiently exert characteristics of polyethylene including resilience.

15 The expanded molded article thus obtained is tough and excellent in impact strength. Furthermore, the expanded molded article has high stiffness due to the modification of styrene.

A falling ball impact value of the expanded molded
20 article is preferably 60 cm or more. The expanded molded article having a falling ball impact value of less than 60 cm may be used, but if the expanded molded article has a falling ball impact value of not less than 60 cm, it is not easily chipped or broken and thus applicable to shipping containers.
25 The falling ball impact value of the expanded molded article is

more preferably 70 cm or more. A method for measuring the falling ball impact value will be described in Examples.

The expanded molded article of the present invention may be used for various purposes, and particularly suitable for
5 material for interior furnishings of a car, energy absorbing material to be inserted inside a bumper, packing material for heavy products, and the like.

Examples

10 The present invention will hereunder be described with reference to Examples and Comparative Examples, but it should be understood that the invention be not limited by these Examples and Comparative Examples. Methods for determining values shown in Examples and Comparative
15 Examples are described below.

(Measurement of powder content)

For measurement of a powder content, about 1000 g of a polymerized slurry sample was introduced into a polymer beaker having a water vent with 35-mesh wire gauze attached
20 on its top. Into this beaker about 6 liter of wash water was gradually introduced, and liquid flowed out of the vent was collected. The collected liquid was filtered by a glass fiber paper filter (GA-100) and dried in an oven at 60°C for 3 hours to measure the weight of dried polymer powder. The resin
25 remained in the slurry sample after washing was dried and

weighed as well. The powder content was determined by the following equation:

$$\frac{\text{Weight of powder resin (g)}}{\text{Weight of dried resin (g)}} \times 100 = \text{powder content (wt\%)}$$

5 (Determination of gel fraction)

For determination of a gel fraction, a sample of resin beads was weighed, the sample was put in a flask, and 100 ml of toluene was added. The beads were then dissolved in a oil bath at 130°C for 24 hours. After the flask was taken out
10 from the oil bath, a resultant mixture was immediately filtered by a 80-mesh (ϕ 0.12 mm) wire gauze, and a sample remaining on the wire gauze which is insoluble in boiling toluene and the wire gauze were then allowed to stand in an oven at 130°C for an hour to remove toluene, and a weight of the resultant solid
15 was measured. The gel fraction is determined by the following equation:

$$\frac{\text{Weight of resultant solid}}{\text{Weight of sample}} \times 100 = \text{gel fraction (wt\%)}$$

About 200 μ g of the resultant solid was weighed and
20 enwrapped in a ferromagnetic metal (Pyrofoil: manufactured by Japan Analytical Industry Co., Ltd.) so as to be in close contact with each other. Then, a pyrolysate was generated using a pyrolysis apparatus called Curie Point Pyrolyzer Model

JHP-3 (manufactured by Japan Analytical Industry Co., Ltd.).
The pyrolysate was analyzed using Gas Chromatograph Auto
System (manufactured by Perkin Elmer) to determine an
polystyrene content from the analytical result. The following
5 analytical conditions were adopted. Pyrolysis temperature:
590 °C-5 sets, oven temperature: 280 °C, needle temperature:
300 °C, column: DB-5 (0.25 μ m \times ϕ 0.25 mm \times 30 m,
manufactured by J & W), column temperature: 50 °C(1 min) \rightarrow
temperature rise of 10 °C/min \rightarrow 100 °C \rightarrow temperature rise of
10 40 °C/min \rightarrow 320 °C(3.5 min), carrier gas: He, carrier flow rate:
1 ml/min, pressure at column inlet: 12 psi, temperature at
column inlet: 300 °C, temperature of a detector: 300 °C, and
detector: FID. Determination was made by an absolute
calibration curve method using polystyrene resin QC254
15 manufactured by Asahi Kasei Co., as a standard sample.

When the polystyrene content is 10 wt% or more, it
was determined that a gel component comprises a graft
polymer but not a cross-linked polymer.

(Measurement of molecular weight of polystyrene resin
20 component in resin beads)

An average molecular weight (M_w) of a polymer was
measured by GPC (Gel Permeation Chromatography) under the
following conditions.

Measuring equipment:

25 High-speed GPC equipment HLC-8020

manufactured by Tosoh Corp.

Column: HSG-60S \times 2, HSG-40H \times 1, HSG-20H \times 1
manufactured by Sekisui Fine Chemicals
Co., Ltd.

5 Measuring conditions:

Column temperature: 40°C

Moving bed: THF (tetrahydrofuran)

Flow rate: 1.0 ml/min

Injection amount: 500ml

10 Detector: RID-6A

manufactured by Tosoh Corp.

Molecular weight determination of the sample:

For measuring a molecular weight of a sample, conditions for
measuring were selected so that a molecular weight

15 distribution of the sample overlaps a range of a linear
calibration curve correlating a count number with a logarithm
of the molecular weight of various monodisperse polystyrene
standard samples. In the present invention, the calibration
curve for polystyrene was plotted using six polystyrene
20 standard samples (TSK standard polystyrene) respectively
having a weight-average molecular weight of 2.74×10^3 , 1.91×10^4 ,
 1.02×10^5 , 3.55×10^5 , 2.89×10^6 , 4.48×10^6 manufactured
by Tosoh Corp.

(Determination of bulk density)

25 A bulk density was determined according to a method

described in JIS K 6911:1955 "General Testing Methods for Thermosetting Plastics". Specifically, pre-expanded beads free-falling into a graduated cylinder by an apparent density measuring instrument was weighed to determine their bulk
5 density by the following equation.

$\text{bulk density (kg/m}^3\text{)} = \text{weight (kg)} / \text{bead volume in the graduated cylinder (m}^3\text{)}$

(Determination of density of expanded molded article)

A density of an expanded molded article was
10 determined according a method described in JIS A 9511:1995 "Preformed Cellular Plastics Thermal Insulation Materials".

(Measurement of impact strength)

For measurement of impact strength, an expanded molded article was cut to form a sample having a size of $215 \times$
15 40×20 mm, and the sample was then placed on a pair of holding members arranged at a distance of 155 mm. A steel ball weighing 321 g was added on the middle of the sample in width direction thereof at a position halfway between the pair of holding members to see whether or not the sample was
20 crushed.

The test was repeated at different heights of drop and the minimum height of drop that produced crush on the sample was defined as a falling ball impact value to evaluate the impact strength. Thus, the impact strength increases as
25 the falling ball impact value increases.

(Measurement of compressive strength)

A compressive strength was measured according to a method described in JIS A 9511:1995 "Preformed Cellular Plastics Thermal Insulation Materials". In other words, the
5 compressive strength of a test specimen having a size of $50 \times 50 \times 50$ mm was measured when it was compressed by 5% using a universal testing machine Tensilon UCT-10T (manufactured by Orientech Co., Ltd.) under a compressive rate of 10 mm/min.

10 (Evaluation of recyclability)

A recyclability was evaluated by extruding styrene-modified polyethylene-based resin beads and an expanded molded article using an extruder (compression kneading uniaxial extruder: CER-40 manufactured by Hoshi Plastic Co.,
15 Ltd., perforated plate: $\phi 2$ mm \times 1 perforation). The number of times strands are cut in an hour was counted. When the strands were cut 5 times or more in an hour, a cross (\times) was marked, and when the strands were cut less than 5 times in an hour, a circle (\circ) was marked. The result of the evaluation
20 was that the \times was marked when a gel fraction was not less than 2 wt%, and the \circ was marked when the gel fraction was less than 2 wt%.

Example 1

(Production of polyethylene-based resin beads)

25 Linear low-density polyethylene (ethylene-hexene

copolymer, melt index of 1.0 g/10 min, density of 0.921 g/ml, melting point of 126 °C) was granulated by an extruder to obtain polyethylene-based resin beads of substantially spherical shape having an L/D of 0.9 and an average bead size of 0.8 mm. As a foam regulator, 0.5 parts by weight of talc relative to 100 parts by weight of the above-mentioned polyethylene was added at the granulation.

(Production of styrene-modified polyethylene-based resin beads)

40 kg of pure water, 200 g of magnesium pyrophosphate as a dispersant, 20 g of sodium dodecylbenzenesulfonate were introduced in an autoclave having an internal volume of 100 liter to prepare an aqueous medium. 14 kg of the above-mentioned polyethylene-based resin beads was suspended in the aqueous medium and stirred at 150 rpm.

Into the autoclave, a mixed solution containing 26 kg of a styrene monomer (185 parts by weight relative to 100 parts by weight of polyethylene) and 78 g of t-butylperoxybenzoate (TBPB) (0.3 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added and allowed to stand at 60 °C for 60 minutes to impregnate the styrene monomer into the polyethylene-based resin beads.

Then, the temperature was raised to 117 °C and

polymerization was performed for 4 hours. Further, by raising to 140 °C and maintained for 2 hours, the remaining monomer was forcibly polymerized to reduce its amount, and then the autoclave was cooled to take out styrene-modified

5 polyethylene-based resin beads. The powder content in the polymerized slurry was 0.3 wt%, and the gel fraction of the resin beads obtained was 0.3 wt%. The polystyrene content in the gel component was 23.3 wt%, and the molecular weight of the polystyrene resin component was about 320,000.

10 (Production of expandable beads of styrene-modified polyethylene-based resin and evaluations of their expandability and moldability)

20 kg of the above-mentioned styrene-modified polyethylene-based resin beads and 400 g of toluene were
15 introduced into a pressure-resistant twin-cylinder mixer which has an internal volume of 50 liter and can be hermetically sealed. After the mixer was hermetically sealed, it was rotated and 2800 g of butane (n-butane: i-butane = 7: 3, volume ratio, butane with the same volume ratio was used in
20 the following Examples) was forced into the mixer. Then, the temperature was raised to 70°C and maintained for 4 hours to impregnate butane into the beads. The mixer was then cooled and expandable beads of a styrene-modified polyethylene-based resin were taken out.

25 The expandable resin beads taken out from the mixer

were immediately pre-expanded by steam to have a bulk density of 33 kg/m³. About 24 hours later, the pre-expanded resin beads were filled into a mold and heated by steam to allow them to fuse together by heat while being expanded, so that an expanded molded article having a density of 33 kg/m³ are obtained. The expanded molded article thus obtained had excellent strength, showing a falling ball impact value as high as 80 cm. The compressive strength was 34 N/cm².

Example 2

40 kg of pure water, 200 g of magnesium pyrophosphate as a dispersant, 20 g of sodium dodecylbenzenesulfonate were introduced in an autoclave having an internal volume of 100 liter to prepare an aqueous medium. 6 kg of the polyethylene-based resin beads obtained in Example 1 was suspended in the aqueous medium and stirred at 150 rpm.

Into the autoclave, a mixed solution containing 12 kg of a styrene monomer (200 parts by weight relative to 100 parts by weight of polyethylene) and 36 g of t-butylperoxy-2-ethylhexylcarbonate (TBPOEHC) (0.3 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added and allowed to stand at 60 °C for 60 minutes to impregnate the styrene monomer into the polyethylene-based resin beads.

Then, the temperature was raised to 115 °C and

polymerization was performed for 3 hours. After a conversion ratio of polymerization of the styrene monomer reached to 85 %, a mixed solution containing 22 kg of a styrene monomer (366 parts by weight relative to 100 parts by weight of polyethylene) and 66 g of TBPOEHC (0.3 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added at 115 °C over a period of 4 hours to perform polymerization while impregnating the styrene monomer into the inside of polyethylene. Then, by raising to 140°C and maintained for 2 hours, the remaining monomer was forcibly polymerized to reduce its amount, and then the autoclave was cooled to take out styrene-modified polyethylene-based resin beads.

The powder content in the polymerized slurry was 0.7 wt%, and the gel fraction of the resin beads obtained was 0.9 wt%. The polystyrene content in the gel component was 22.2 wt%, and the molecular weight of the polystyrene resin component was about 320,000. The expandable resin beads taken out from the mixer were immediately pre-expanded by steam to have a bulk density of 33 kg/m³ as in Example 1. As in Example 1, the pre-expanded resin beads was expanded and molded to obtain an expanded molded article. The expanded molded article had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 70 cm. The compressive strength was 42 N/cm².

Example 3

The same polymerization procedure as in Example 1 was repeated except that the amounts of the polyethylene-based resin beads, styrene monomer and TBPB were 20 kg, 20 kg (100 parts by weight relative to 100 parts by weight of polyethylene) and 60 g (0.3 parts by weight relative to 100 parts by weight of the styrene monomer), respectively, and that the temperature for polymerization was 115 °C, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article thereof.

The powder content in the polymerized slurry was 0.3 wt%, and the gel fraction of the resin beads obtained was 0.6 wt%. The polystyrene content in the gel component was 25.0 wt%, and the molecular weight of the polystyrene resin component was about 300,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 90 cm. The compressive strength was 30 N/cm².

Example 4

The same polymerization procedure as in Example 1 was repeated except that dicumyl peroxide (DCP) was adopted as the polymerization initiator and that the temperature for polymerization was 130 °C, to obtain styrene-modified

polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article thereof.

The powder content in the polymerized slurry was 0.6 wt%, and the gel fraction of the resin beads obtained was 0.8 wt%. The polystyrene content in the gel component was 18.7 wt%, and the molecular weight of a polystyrene resin component was about 270,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 85 cm. The compressive strength was 35 N/cm².

Example 5

The same polymerization procedure as in Example 1 was repeated except that 156 g of t-butylperoxy-3, 5, 5-trimethylhexanoate (TBPOTMH) (0.6 parts by weight relative to 100 parts by weight of the styrene monomer) was adopted as the polymerization initiator, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article thereof.

The powder content in the polymerized slurry was 0.3 wt%, and the gel fraction of the resin beads obtained was 0.4 wt%. The polystyrene content in the gel component was 25.0 wt%, and the molecular weight of the polystyrene resin component was about 250,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article

obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 80 cm. The compressive strength was 32 N/cm².

Example 6

5 The same polymerization procedure as in Example 1 was repeated except that the amounts of the polyethylene-based resin beads and styrene monomer were 11.5 kg and 28.5 kg (250 parts by weight relative to 100 parts by weight of polyethylene), respectively, to obtain
10 styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article thereof.

 The powder content in the polymerized slurry was 0.8 wt%, and the gel fraction of the resin beads obtained was 0.7
15 wt%. The polystyrene content in the gel component was 15.7 wt%, and the molecular weight of the polystyrene resin component was about 320,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article obtained had a density of 33 kg/m³ and was excellent in
20 strength, showing a falling ball impact value as high as 80 cm. The compressive strength was 36 N/cm².

Example 7

 40 kg of pure water, 200 g of magnesium pyrophosphate as a dispersant, 20 g of sodium
25 dodecylbenzenesulfonate were introduced in an autoclave

having an internal volume of 100 liter to prepare an aqueous medium. 10 kg of the polyethylene-based resin beads obtained in Example 1 was suspended in the aqueous medium and stirred at 150 rpm.

5 Into the autoclave, a mixed solution containing 4 kg of a styrene monomer (40 parts by weight relative to 100 parts by weight of polyethylene) and 12 g of DCP (0.3 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added and allowed to stand at
10 60 °C for 60 minutes to impregnate the styrene monomer into the polyethylene-based resin beads.

 Then, the temperature was raised to 130 °C and polymerization was performed for 3 hours. After a conversion ratio of polymerization of the styrene monomer reached to 90 %,
15 a mixed solution containing 26 kg of a styrene monomer (260 parts by weight relative to 100 parts by weight of polyethylene) and 78 g of TBPOEHC (0.3 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added at 115 °C over a period of 4 hours to perform
20 polymerization while impregnating styrene into the inside of polyethylene. Then, by raising to 140°C and maintained for 2 hours, the remaining monomer was forcibly polymerized to reduce its amount, and then the autoclave was cooled to obtain styrene-modified polyethylene-based resin beads. Also, as in
25 Example 1, a pre-expanded resin beads and an expanded

molded article was obtained.

The powder content in the polymerized slurry was 0.6 wt%, and the gel fraction of the resin beads obtained was 0.5 wt%. The polystyrene content in the gel component was 16.0 wt%, and the molecular weight of the polystyrene resin component was about 320,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article obtained in the same manner as in Example 1 had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 75 cm. The compressive strength was 38 N/cm².

Example 8

40 kg of pure water, 200 g of magnesium pyrophosphate as a dispersant, 20 g of sodium dodecylbenzenesulfonate were introduced in an autoclave having an internal volume of 100 liter to prepare an aqueous medium. 4.4 kg of the polyethylene-based resin beads obtained in Example 1 was suspended in the aqueous medium and stirred at 150 rpm.

Into the autoclave, a mixed solution containing 4.4 kg of a styrene monomer (100 parts by weight relative to 100 parts by weight of polyethylene) and 13.2 g of DCP (0.3 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added and allowed to stand at 60 °C for 60 minutes to impregnate the styrene

monomer into the polyethylene-based resin beads.

Then, the temperature was raised to 130 °C and polymerization was performed for 3 hours. After a conversion ratio of polymerization of the styrene monomer reached to 90 %, a mixed solution containing 31.2 kg of a styrene monomer (700 parts by weight relative to 100 parts by weight of polyethylene) and 93.6 g of TBPOEHC (0.3 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added at 115 °C over a period of 5 hours to perform polymerization while impregnating styrene into the inside of polyethylene. Then, by raising to 140°C and maintained for 2 hours, the remaining monomer was forcibly polymerized to reduce its amount, and then the autoclave was cooled to obtain styrene-modified polyethylene-based resin beads. Also, as in Example 1, a pre-expanded resin beads and an expanded molded article was obtained.

The powder content in the polymerized slurry was 0.9 wt%, and the gel fraction of the resin beads obtained was 0.8 wt%. The polystyrene content in the gel component was 15.0 wt%, and the molecular weight of the polystyrene resin component was about 320,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article obtained in the same manner as in Example 1 had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 65 cm. The compressive strength was

45 N/cm².

Example 9

40 kg of pure water, 200 g of magnesium pyrophosphate as a dispersant, 20 g of sodium

5 dodecylbenzenesulfonate were introduced in an autoclave having an internal volume of 100 liter to prepare an aqueous medium. 14 kg of the polyethylene-based resin beads obtained in Example 1 was suspended in the aqueous medium and stirred at 150 rpm.

10 Into the autoclave, a mixed solution containing 5.6 kg of a styrene monomer (40 parts by weight relative to 100 parts by weight of polyethylene) and 13.4 g of DCP (0.24 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added and allowed to stand at
15 60 °C for 60 minutes to impregnate the styrene monomer into the polyethylene-based resin beads.

Then, the temperature was raised to 130 °C and polymerization was performed for 3 hours. After a conversion ratio of polymerization of the styrene monomer reached to 90 %,
20 a mixed solution containing 20.4 kg of a styrene monomer (145 parts by weight relative to 100 parts by weight of polyethylene) and 49 g of TBPOEHC (0.24 parts by weight relative to 100 parts by weight of the styrene monomer) as a polymerization initiator was added at 117 °C over a period of 4 hours to
25 perform polymerization while impregnating styrene into the

inside of polyethylene. Then, by raising to 140°C and maintained for 2 hours, the remaining monomer was forcibly polymerized to reduce its amount, and then the autoclave was cooled to obtain styrene-modified polyethylene-based resin beads. Also, as in Example 1, a pre-expanded resin beads and an expanded molded article was obtained.

The powder content in the polymerized slurry was 0.2 wt%, and the gel fraction of the resin beads obtained was 0.3 wt%. The polystyrene content in the gel component was 16.6 wt%, and the molecular weight of the polystyrene resin component was about 320,000. The pre-expanded resin beads and expanded molded article obtained in the same manner as in Example 1 had a bulk density of 33 kg/m³ and a density of 33 kg/m³, respectively, and was excellent in strength, showing a falling ball impact value as high as 80 cm. The compressive strength was 35 N/cm².

Comparative Example 1

The same polymerization procedure as in Example 1 was repeated except that the amounts of the polyethylene-based resin beads and styrene monomer were 31 kg and 9 kg (30 parts by weight relative to 100 parts by weight of polyethylene), respectively, and that 27 g of TBPOTMH was adopted as the polymerization initiator, to obtain styrene-modified polyethylene-based resin beads.

The powder content in the polymerized slurry was 0.6

wt%, and the gel fraction of the resin beads obtained was 2.1 wt%. The polystyrene content in the gel component was 23.8 wt%. The same procedure as in Example 1 was repeated to obtain a pre-expanded resin beads and an expanded molded article, but due to poor retention of gas, the pre-expanded resin beads having a bulk density of 33 kg/m³ and the expanded molded article having a density of 33 kg/m³ could not be obtained.

Comparative Example 2

The same polymerization procedure as in Example 1 was repeated except that the temperature for polymerization was 119 °C, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article. The powder content in the polymerized slurry was 0.7 wt%, and the gel fraction of the resin beads was 6.5 wt%. The polystyrene content in the gel component was 21.5 wt%, and the molecular weight of the polystyrene resin component was about 270,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. An expanded molded article obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 90 cm. However, due to the high gel fraction of the resin beads, recycled use of the expanded molded article was difficult. The compressive strength was 38 N/cm².

Comparative Example 3

The same polymerization procedure as in Example 1 was repeated except that the temperature for polymerization was 121 °C, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded
5 molded article. The powder content in the polymerized slurry was 0.8 wt%, and the gel fraction of the resin beads was 25.0 wt%. The polystyrene content in the gel component was 24.0 wt%, and the molecular weight of the polystyrene resin component was about 260,000. The pre-expanded resin beads
10 had a bulk density of 33 kg/m³. The expanded molded article obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 100 cm. However, due to the high gel fraction of the resin beads, recycled use of the expanded molded article was difficult. The
15 compressive strength was 40 N/cm².

Comparative Example 4

The same polymerization procedure as in Example 1 was repeated except that the temperature for polymerization was 122 °C, to obtain styrene-modified polyethylene-based
20 resin beads, a pre-expanded resin beads and an expanded molded article. The powder content in the polymerized slurry was 0.7 wt%, and the gel fraction of the resin beads obtained was as high as 32.2 wt%. The polystyrene content in the gel component was 26.4 wt%, and the molecular weight of the
25 polystyrene resin component was about 250,000. The

pre-expanded resin beads had a bulk density of 33 kg/m³. An expanded molded article obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 100 cm. However, due to the high gel fraction of the resin beads, recycled use of the expanded molded article was difficult. The compressive strength was 42 N/cm².

Comparative Example 5

The same polymerization procedure as in Example 1 was repeated except that the temperature for polymerization was 123 °C, to obtain styrene-modified polyethylene-based resin beads a pre-expanded resin beads and an expanded molded article. The powder content in the polymerized slurry was 0.6 wt%, and the gel fraction of the resin beads was 19.6 wt%. The polystyrene content in the gel component was 26.5 wt%, and the molecular weight of the polystyrene resin component was about 260,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 95 cm. However, due to the high gel fraction of the resin beads, recycled use of the expanded molded article was difficult. The compressive strength was 40 N/cm².

Comparative Example 6

The same polymerization procedure as in Example 1

was repeated except that the temperature for polymerization was 125 °C, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article. The powder content in the polymerized slurry
5 was 0.5 wt%, and the gel fraction of the resin beads obtained was 4.6 wt%. The polystyrene content in the gel component was 23.9 wt%, and the molecular weight of the polystyrene resin component was about 260,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. An expanded molded
10 article obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 90 cm. However, due to the high gel fraction of the resin beads, recycled use of the expanded molded article was difficult. The compressive strength was 38 N/cm².

15 Comparative Example 7

The same polymerization procedure as in Example 1 was repeated except that the temperature for polymerization was 135 °C, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded
20 molded article. The powder content in the polymerized slurry was 0.5 wt%, and the gel fraction of the resin beads was 5.2 wt%. The polystyrene content in the gel component was 25.0 wt%, and the molecular weight of the polystyrene resin component was about 220,000. The pre-expanded resin beads
25 had a bulk density of 33 kg/m³. An expanded molded article

obtained had a density of 33 kg/m³ and was excellent in strength, showing a falling ball impact value as high as 90 cm. However, due to the high gel fraction of the resin beads, recycled use of the expanded molded article was difficult. The
5 compressive strength was 38 N/cm².

Comparative Example 8

The same polymerization procedure as in Comparative Example 2 was repeated except that the amount of the polymerization initiator was 312 g (1.2 parts by weight relative
10 to 100 parts by weight of the styrene monomer), to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article. The powder content in the polymerized slurry was 0.6 wt%, and the gel fraction of the resin beads was 4.5 wt%. The
15 polystyrene content in the gel component was 22.2 wt%, and the molecular weight of the polystyrene resin component was as low as about 150,000, suggesting that the styrene monomer was not uniformly polymerized in polyethylene. The pre-expanded resin beads had a bulk density of 33 kg/m³.
20 The expanded molded article obtained had a density of 33 kg/m³. The expanded molded article was poor in strength, showing a falling ball impact value of 35 cm, possibly due to the non-uniform polymerization of the styrene monomer in polyethylene. The compressive strength was 28 N/cm². Also,
25 recycled use of the expanded molded article was difficult.

Comparative Example 9

The same polymerization procedure as in Comparative Example 8 was repeated except that the temperature for polymerization was 117 °C, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article thereof. The powder content in the polymerized slurry was 0.6 wt%, and the gel fraction of the resin beads obtained was 0.9 wt%. The polystyrene content in the gel component was 17.7 wt%, and the molecular weight of the polystyrene resin component was about 160,000. The pre-expanded resin beads had a bulk density of 33 kg/m³. The expanded molded article obtained had a density of 33 kg/m³ and was poor in strength, showing a falling ball impact value as low as 40 cm. The compressive strength was 28 N/cm².

A ratio between materials and the polymerization conditions of Examples 1 to 9 and Comparative examples 1 to 9 are shown in Table 1. The powder content, gel fraction, polystyrene content, molecular weight of the polystyrene resin component, falling ball impact value, compressive strength, and recyclability are together shown in Table 2.

Table 1

	PE/PS pbw Ratio	Conversion Ratio of Polymerization (%)	Polymerization Temperature (°C)	Polymerization Initiator	Amount of Initiator (pbw)
Ex. 1	100/185	—	117	TBPB	0.3
Ex. 2	100/566	85	115	TBPOEHC	0.3
Ex. 3	100/100	—	115	TBPB	0.3
Ex. 4	100/185	—	130	DCP	0.3
Ex. 5	100/185	—	117	TBPOTMH	0.6
Ex. 6	100/250	—	117	TBPB	0.3
Ex. 7	100/300	90	130, 115	DCP, TBPOEHC	0.3, 0.3
Ex. 8	100/800	90	130, 115	DCP, TBPOEHC	0.3, 0.3
Ex. 9	100/185	90	130, 117	DCP, TBPOEHC	0.24, 0.24
Comp. Ex. 1	100/30	—	117	TBPOTMH	0.3
Comp. Ex. 2	100/185	—	119	TBPB	0.3
Comp. Ex. 3	100/185	—	121	TBPB	0.3
Comp. Ex. 4	100/185	—	122	TBPB	0.3
Comp. Ex. 5	100/185	—	123	TBPB	0.3
Comp. Ex. 6	100/185	—	125	TBPB	0.3
Comp. Ex. 7	100/185	—	135	TBPB	0.3
Comp. Ex. 8	100/185	—	119	TBPB	1.2
Comp. Ex. 9	100/185	—	117	TBPB	1.2

Table 2

	Powder Content (wt%)	Gel Fraction (wt%)	PS Content in Gel Component (wt%)	M.W. Ca. ($\times 10^4$)	Falling Ball Impact Value (cm)	Compressive Strength (N/cm ²)	Recyclability
Ex. 1	0.3	0.3	23.3	32	80	34	○
Ex. 2	0.7	0.9	22.2	32	70	42	○
Ex. 3	0.3	0.6	25.0	30	90	30	○
Ex. 4	0.6	0.8	18.7	27	85	35	○
Ex. 5	0.3	0.4	25.0	25	80	32	○
Ex. 6	0.8	0.7	15.7	32	80	36	○
Ex. 7	0.6	0.5	16.0	32	75	38	○
Ex. 8	0.9	0.8	15.0	32	65	45	○
Ex. 9	0.2	0.3	16.6	32	80	35	○
Comp. Ex. 1	0.6	2.1	23.8	30	—	—	—
Comp. Ex. 2	0.7	6.5	21.5	27	90	38	×
Comp. Ex. 3	0.8	25.0	24.0	26	100	40	×
Comp. Ex. 4	0.7	32.2	26.4	25	100	42	×
Comp. Ex. 5	0.6	19.6	26.5	26	95	40	×
Comp. Ex. 6	0.5	4.6	23.9	26	90	38	×
Comp. Ex. 7	0.5	5.2	25.0	22	90	38	×
Comp. Ex. 8	0.6	4.5	22.2	15	35	28	×
Comp. Ex. 9	0.6	0.9	17.7	16	40	28	○

Example 10

Polyethylene-based resin beads were obtained in the same manner as in Example 1 except that linear low-density polyethylene (ethylene-butene copolymer: melt index of 0.7 g/10 min, density of 0.922/ml, melting point of 121 °C) different in melting point from that of Example 1 was used.

The same polymerization procedure as in Example 1 was repeated except that the above-mentioned polyethylene-based resin beads and TBPOTMH as the polymerization initiator were used and that the temperature for polymerization was 111 °C, to obtain styrene-modified polyethylene-based resin beads.

The powder content in the polymerized slurry was 0.6 wt%, and the gel fraction of the resin beads obtained was 0.5 wt%. The polystyrene content in the gel component was 16.0 wt%, and the molecular weight of the polystyrene resin component was about 380,000. A pre-expanded resin beads and expanded molded article obtained in the same manner as in Example 1 had a bulk density of 33 kg/m³ and density of 33 kg/m³, respectively, and was excellent in strength, showing a falling ball impact value as high as 80 cm and a compressive strength as high as 34 N/cm².

Example 11

Polyethylene-based resin beads were obtained in the same manner as in Example 1 except that linear low-density

polyethylene (ethylene-butene copolymer: melt index of 0.7 g/10 min, density of 0.922/ml, melting point of 121 °C) having a different melting point from that used in Example 1 was used.

5 The same polymerization procedure as in Example 1 was repeated except that the above-mentioned polyethylene-based resin beads and DCP as the polymerization initiator were used and that the temperature for polymerization was 124 °C, to obtain styrene-modified polyethylene-based
10 resin beads.

 The powder content in the polymerized slurry was 0.5 wt%, and the gel fraction of the resin beads obtained was 0.8 wt%. The polystyrene content in the gel component was 15.0 wt%, and the molecular weight of the polystyrene resin
15 component was about 270,000. A pre-expanded resin beads and expanded molded article obtained in the same manner as in Example 1 had a bulk density of 33 kg/m³ and density of 33 kg/m³, respectively, and was excellent in strength, showing a falling ball impact value as high as 85 cm and a compressive
20 strength as high as 35 N/cm².

 The polymerization conditions, powder content, gel fraction, polystyrene content, molecular weight of the polystyrene resin component, falling ball impact value, compressive strength and recyclability of Examples 10 and 11
25 are together shown in Table 3

Table 3

Polymeri- zation Temp. (°C)	Polymeri- zation Initiator	Amount of Initiator (pbw)	Powder Content (%)	Gel Fraction (%)	PS Content in Gel (wt%)	M.W. Ca. ($\times 10^4$)	Falling Ball Impact Value (cm)	Compressive Strength (N/cm ²)	Recycl- ability
111	TBPOTMH	0.3	0.6	0.5	16.0	38	80	34	○
124	DCP	0.3	0.5	0.8	15.0	27	85	35	○

As seen in Table 3, it is understood that, even when the polyethylene-based resin having the different melting point is used, a smaller amount of gel component is generated as long as the polymerization temperature is in a range of the present invention.

Example 12

The same polymerization procedure as in Example 1 was repeated except that 183 parts by weight of a styrene monomer and 2 parts by weight of α -methyl styrene (α -MS) relative to 100 parts by weight of polyethylene were added, to obtain styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article thereof.

The powder content in the polymerized slurry was 0.8 wt%, and the gel fraction of the resin beads obtained was 0.9 wt%. The polystyrene content in the gel component was 17.8 wt%, and the molecular weight of the polystyrene resin component was about 250,000. The pre-expanded resin beads and expanded molded article obtained in the same manner as in Example 1 had a bulk density of 33 kg/m³ and density of 33 kg/m³, respectively, and was excellent in strength, showing a falling ball impact value as high as 75 cm. The compressive strength was 32 N/cm².

A ratio between materials, the polymerization conditions, powder content, gel fraction, polystyrene content,

molecular weight of the polystyrene resin component, falling ball impact value, compressive strength and recyclability of Example 12 are together shown in Table 4.

Table 4

PE/ PS/ α -MS	Polymeri- zation Temp. (°C)	Polymeri- zation Initiator	Amount of Initiator (pbw)	Powder Content (%)	Gel Fraction (%)	PS Content In Gel (wt%)	M.W. Ca. ($\times 10^4$)	Falling Ball Impact Value (cm)	Compressive Strength (N/cm ²)	Recycl- ability
100/183/2	117	TBPB	0.3	0.8	0.9	17.8	25	75	32	O

As seen in Table 4, it is understood that, even when a mixture of two different kinds of styrene monomers is used, a smaller amount of gel component is generated as long as the polymerization temperature is in a range of the present

5 invention

Example 13

Styrene-modified polyethylene-based resin beads, a pre-expanded resin beads and an expanded molded article thereof were obtained in the same manner as in Example 1
10 except that different polymerization temperatures and initiators shown in Table 5 were adopted for studying a relationship between the polymerization temperature and the gel fraction. The polymerization temperature, type of the polymerization initiator, gel fraction, polystyrene content in
15 the gel component, molecular weight of the polystyrene resin component, falling ball impact value, compressive strength and recyclability are together shown in Table 5. Also, the relationship between the polymerization temperature and the gel fraction is shown in Fig. 1.

Table 5

Polymerization Temperature (°C)	Polymerization Initiator	Gel Fraction (%)	PS Content in Gel Component (wt%)	Powder Content (%)	M.W. Ca. ($\times 10^4$)	Falling Ball Impact Value (cm)	Compressive Strength (N/cm ²)	Recyclability
110	TBPO TMH	0.6	16.6	0.5	38	50	35	○
112	TBPO TMH	0.8	13.7	0.4	38	80	34	○
114	TBPO TMH	0.5	18.0	0.4	36	80	34	○
115	TBPB	0.3	23.3	0.5	35	80	35	○
116	TBPB	0.7	14.3	0.5	33	80	35	○
117	TBPB	0.3	23.3	0.3	32	80	34	○
118	TBPB	1.8	17.7	0.6	30	85	36	○
119	TBPB	6.5	21.5	0.7	27	90	38	×
120	TBPB	18	20.0	0.7	28	100	40	×
121	TBPB	25	24.0	0.8	26	100	40	×
122	TBPB	32.2	26.4	0.7	25	100	42	×
123	DCP	19.6	26.5	0.6	26	95	40	×
124	DCP	20.1	24.4	0.7	26	100	42	×
125	DCP	4.6	23.9	0.5	26	90	38	×
126	DCP	2.6	20.0	0.6	27	85	38	×
128	DCP	1.6	18.7	0.5	26	85	36	○
130	DCP	0.8	18.7	0.6	27	85	35	○
132	DCP	2.4	37.5	0.6	25	85	36	×
135	DCP	5.2	25.0	0.5	22	90	38	×

As seen in Table 5 and Fig. 1, it is understood that the gel fraction is remarkably decreased when the polymerization temperature is in the range of the present invention (112 to 118 °C and 128 to 130 °C). When the
5 polymerization temperature was 110 °C which is 16 °C lower than the melting point of the polyethylene-based resin, the gel fraction was not more than 2 wt%. However, the falling ball impact value was low, probably because due to insufficient polymerization of styrene.

10

As described hereinbefore, the present invention includes the step of impregnating the styrene-based monomer into the polyethylene-based resin beads for polymerization at a specific temperature, thereby realizing uniform impregnation of
15 the styrene-based monomer into the polyethylene-based resin beads and uniform polymerization of the styrene-based monomer. Consequently, the present invention provides the expandable resin beads which provide the expanded molded article excellent in physical properties and particularly having
20 an excellent impact resistance. Further, the expanded molded article obtained by using the expandable resin beads of the invention is readily recycled since the generation of the gel component derived from the cross-linking or graft polymerization is reduced. Still further, since the expandable
25 resin beads of the invention are produced by impregnating the

styrene-based monomer into the inside of polyethylene for polymerization, adding an additional styrene-based monomer while the polymerization of the styrene-based monomer is proceeding to a certain degree, and then simultaneously performing the impregnation and polymerization at a specific temperature, the expandable resin beads have less generation of the polymer powder and maintain a high content of the polystyrene resin component.